GRÜNWALD'S MATHEMATICAL SPECTRUM ANALYSIS.

THE following interesting criticism of Dr. Grünwald's recent work on the mathematical spectrum analysis of various of the elements, by Joseph S. Ames, of the Johns Hopkins University, appears in the February number of the *American Chemical Journal*:—

"Dr. Anton Grünwald, Professor of Mathematics in the Technical High School at Prague, has given his theory of spectrum analysis in the following papers:—(1) 'Ueber das Wasserspectrum, das Hydrogen-, und Oxygenspectrum,' *Astronomische Nachrichten*, No. 2797, 1887, and *Phil. Mag.*, xxiv. 354, 1887; (2) 'Math. Spectralanalyse des Magnesiums und der Kohle,' *Monatshefte für Chemie*, viii. 650, *Wiener Sitz. Berichte*, 2 Abth. xcvi., 1887; *Phil. Mag.*, xxv. 343, 1888 (abstract); and (3) 'Math. Spectralanalyse des Kadmiums,' *Monatshefte für Chemie*, ix. 956.

"His aim is to discover relations between the elements by tracing connections between their spectra, and thus to arrive at simpler, if not fundamental, 'elements.' He considers the lines in the spectra of two substances, say A and B. If he finds a group of lines in the spectrum of A, which, on multiplication with a simple numerical factor, give line for line a group in the spectrum of B, he assumes that A and B have a common component. This factor, which transforms the one group into the other, is, he says, the ratio of the volumes occupied by the common constituent in unit volume of the two substances. Thus, let *c* be common to A and B, and let it occupy the volume [*a*] in unit volume of A, and [*b*] in unit volume of B; then the factor which transforms that part of the spectrum of A due to *c* into that of B, also due to *c*, is [*b*]/[*a*]. It is not difficult to find relations between the spectra of different substances; and, accepting Dr. Grünwald's hypothesis as to the transforming factor, we can deduce formulas for the elements. For example, in the hydrogen spectrum there are two groups of lines, [*a*] and [*b*], which, when multiplied respectively by $\frac{19}{30}$ and $\frac{4}{5}$, give corresponding groups in the spectrum of water, and, since in water hydrogen occupies $\frac{2}{3}$ of the volume, we have the equations

$$[a] + [b] = 1$$
$$\tfrac{19}{30}[a] + \tfrac{4}{5}[b] = \tfrac{2}{3}$$
$$\therefore [a] = \tfrac{4}{5}, \quad [b] = \tfrac{1}{5}$$

which gives hydrogen the composition ba_4. For reasons which depend upon solar physics, Grünwald calls the substance *a* coronium, and *b* helium. Further, he says that all the lines in Hasselberg's secondary spectrum of hydrogen can be changed into water-line by multiplying by $\frac{1}{2}$; which shows, according to his theory, that the modified molecule H^1 occupies in H_2O half the volume it does in the free condition. He finds that oxygen has the composition $H^1b_4(b_4c_5)_5$, where *c* is a new substance. In his last paper, however, Dr. Grünwald states that he has proved *c* to be nothing but *a* in a different state of compression.

"He adopts the spectrum of water, *i.e.* of the oxyhydrogen flame, as a standard, and is then able to give various criteria by means of which the primary elements *a* and *b* may be recognized. Among them are the following: If λ is the wave-length of any line produced by *a* as it exists in hydrogen, $\frac{19}{30}\lambda$, $\frac{3}{4}\lambda$, $\frac{56}{75}\lambda$ will each be the wave-lengths of any line of the water-spectrum, and if λ is the wave-length of any line produced by *b* as it exists in hydrogen, $\frac{4}{5}\lambda$ will be the wave-length of a line of the water-spectrum. Applying his criteria to magnesium, carbon, and cadmium, he finds that they are made up entirely of *a* and *b* in various states of compression. For instance, one group of lines in the cadmium spectrum is transformed into a group of *b* by the factor $\frac{2}{3}$, another group is identical with a group of *b*, and so on. But the group of lines of *shortest* wave-length is transformed into a group of *b* by the factor $\frac{7}{6}$; and cadmium falls in the seventh row of Mendelejeff's table. Similarly, the group of lines of shortest wave-length of zinc is transformed into a group of *b* by the factor $\frac{5}{4}$, and zinc is in the fifth row of the table. Dr. Grünwald finds in this a general law which he verifies in the cases of Al, Si, Fe, Cu, Zn, As, Sr, Ag, Cd, In, Sn, Sb, Te, Ba, Au, Hg, Tl, Pb, and Bi. He farther connects the lines of greater wave-length with the substance *a*; and, as in all cases so far tried all the lines can be deduced from these two substances, he is led to believe that *all the so called elements are compounds of the primary elements a and b.*

"It is unfortunate that Dr. Grünwald has not published a complete list of the lines characteristic of *a* and *b*, for until this is done his theory cannot be accurately tested. There are two distinct questions to be answered: (1) Are there any numerical relations connecting the spectra of the elements? and if so, (2) what is the meaning of the fact? Cornu, Deslandres, and others have long since answered the first question for us, but whether Dr. Grünwald's answer to the second is correct or not depends upon the completeness with which the numerical relations hold for the *entire* spectra of the substances. It is here that Dr. Grünwald's work can be criticized.

"As noted above, the spectrum of the oxyhydrogen flame is used to test the existence of lines belonging to *a* and *b*. By far the most accurate and complete determination of this spectrum is that of Liveing and Dewar (Phil. Trans. 1888); but this does not always answer Dr. Grünwald's purposes. In the B. A. Report for 1886 there is a provisional list of lines of the water-spectrum, which he often uses, although the wave-lengths have since been corrected. Further, if other lines are necessary, they are found by halving the wave-lengths of the secondary spectrum of hydrogen. Many lines thus determined are actually present in the water-spectrum; but why are not *all* there? Dr. Grünwald says it is because the amplitude of vibrations of parts of the molecule can be so changed, owing to the presence of other substances, that the intensity may increase or diminish, or become too faint to be observed. To this argument there is absolutely no answer. In some cases, too, the average of two wave-lengths is used as a criterion of a wave-length of *b* which falls between them! And as a last resort, if the necessary wave-length cannot be found in the water-spectrum by any of these means, it is put down as 'new,' and is called an 'unobserved' line. As just shown, Dr. Grünwald easily explains why the strongest lines in the spectrum of an element, cadmium for example, when 'transformed' into water-lines, may be faint, and *vice versâ*. But how does he account for the fact that double lines are not transformed into double lines? This seems to me a fundamental objection. The concave-grating gives the only accurate method of determining the ultra-violet wave-lengths of the elements; and, as a consequence of not using it, most of the tables of wave-lengths so far published are not of much value. So Grünwald's error here may be great. And, besides, when we consider that in the water-spectrum as given by Liveing and Dewar, without the help of the secondary spectrum of hydrogen, there is on the average one line for every two Ångström units, it would be remarkable indeed if any law could not be verified. This is strikingly shown in the first group of the cadmium lines. Here 6742 and 6740 are two readings for the wave-lengths of the *same* line, as made by two observers; yet Grünwald finds a water-line for each of them!

"The fact that there are exact numerical relations connecting the spectra of different elements does not afford a proof of Grünwald's hypothesis; and until the above difficulties are removed the evidence is against it. But, even granting it, how do we know that *a* and *b* are not themselves compounds? In the second group of cadmium lines there are nineteen lines which can be transformed into *b* lines; *b* has many other lines; so at the most this only shows that cadmium and *b* have a common constituent unless, of course, the absence of the other cadmium lines is accounted for in Grünwald's own way of varying intensity.

"The lines of the spectrum of any substance, as carbon or iron, seem to fall into definite series or groups; and the wave-lengths of the lines in these groups can be expressed by formulas, as is well known. All that the fact of there being a connection between the spectra of different substances seems to show is, then, that there may be a formula common to many elements, as Kayser and Runge have recently found. And all that this means is that the molecules of those elements vibrate in general according to a similar law."

ON THE FORMATION OF MARINE BOILER INCRUSTATIONS.[1]

IN the older forms of marine boilers, sea water was almost universally employed; but with the introduction of high-pressure tubular boilers the amount of deposit was so serious, and the difficulty of removing it so great, that it became imperative to use distilled water. It is found, however, that the trouble has

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[1] A Paper read at the thirtieth session of the Institution of Naval Architects, by Prof. Vivian B. Lewes, F.C.S., F.I.C., Royal Naval College, on April 11, 1889.

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only been transferred from the steam boilers to the distilling apparatus, and that constant breakdowns of the latter necessitate the introduction of sea water into the boiler to eke out the supply of distilled water from the condensers.

The waters at present in use in marine boilers may be classified as—

(1) Sea water, (2) distilled water, (3) mixtures of sea water with distilled or fresh water.

In this paper the nature and causes of the deposits are studied in each of these cases.

Fresh water contains about twenty to fifty grains per gallon of dissolved solids, principally consisting of calcium carbonate, held in solution by carbonic acid present in the water, whilst sea water contains about 2300 grains per gallon, consisting principally of sodium chloride, together with magnesium salts and calcium sulphate. The wide difference in composition between fresh and sea water is also shown in the deposits formed by them. Analyses show that with fresh water the incrustation may be looked upon as consisting principally of calcium carbonate; that with a mixture of fresh and salt water the deposit consists of nearly equal parts of calcium carbonate and calcium sulphate; whilst the sea water gives practically calcium sulphate.

A deposit of calcium carbonate only, separates out as a soft powder, which remains suspended in the water for some time, and can fairly easily be removed from the boiler on cleaning; whilst calcium sulphate as formed in the boiler separates out in a crystalline form, and binds the deposit into a hard mass, so hard in fact that it requires the aid of a chisel and hammer to detach it from the plates and tubes, an operation which is extremely injurious, and tends to shorten the life of the boiler.

Calcium sulphate is much more soluble in a saline solution such as sea water than it is in fresh water, but its solubility rapidly decreases (1) on concentration of the saline solution, and (2) with increase of temperature and pressure.

Sea water having a density of 1·027 was evaporated, and analyses made at different densities with the following results:—

Saline Constituents per Cent.

Density ...	1·029	1·05	1·09	1·225
Sodic chloride	2·6521	4·4201	7·9563	23·8689
Calcic sulphate ...	0·1305	0·2175	0·3915	none
Calcic carbonate ...	0·0103	0·0171	none	none
Magnesic carbonate ...	0·0065	0·0032	none	none
Magnesic chloride ...	0·2320	0·3865	0·6960	2·0880
Magnesic sulphate ...	0·1890	0·3150	0·5670	1·7010

So that on concentrating sea water at ordinary atmospheric pressure, three distinct stages may be traced:—

(1) Deposition of basic magnesic carbonate;

(2) Deposition of calcic carbonate with remaining traces of the basic magnesic carbonate and hydrate; and, finally,

(3) Deposition of the calcic sulphate.

If the sea water be heated and concentrated above a density of 1·225, the salt commences to crystallize out.

These experiments show that if sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1·09) to prevent the deposition of the calcium sulphate; but any such regulation of density is rendered abortive by the fact that pressure and consequent raising of the boiling-point acts upon the calcium sulphate in solution in exactly the same way as concentration, as it is found that this substance is perfectly insoluble in either sea or fresh water at a temperature of 150° C. In the present high-pressure boilers, even if the sea water be mixed with a hundred times its volume of distilled water, so as to reduce its density very low, deposition of calcium sulphate still occurs.

Analyses of several specimens of deposits from boilers where sea water was used, showed that in all cases there were two distinct layers—(1) a hard crystalline deposit on the sides of the tubes, consisting of nearly pure calcium sulphate in the form of "anhydrite"; (2) a softer portion resembling alabaster in the interior, consisting of calcium sulphate, with about 6 per cent. of magnesic hydrate.

The presence of magnesic hydrate in boiler deposits is supposed to be due to the mutual decomposition of water and magnesic chloride, later experiments have shown, however, that when magnesic chloride and calcium carbonate mutually react upon each other, soluble calcium chloride and magnesium hydrate are formed; this explains why calcium carbonate is never found, except in very small quantities in marine boiler deposits.

When distilled water only is used, a slight coating is formed, practically consisting only of organic matter, whilst if at any time through a break-down in the distilling apparatus sea water is mixed with the distilled water, a thin and very hard scale of calcic sulphate is formed. An incrustation of this character gave on analysis:—

Calcic sulphate	90·84
Magnesic hydrate	0·75
Sodic chloride	1·41
Silica	0·85
Copper carbonate	1·11
Oxides of iron and alumina	0·24
Organic matter	2·96
Moisture	1·84
	100·00

This scale is of great interest from the presence in it of the carbonate of copper. It is well known that distilled water has a far greater solvent effect upon metals than a water containing salts in solution, and it is quite conceivable that the distilled water from the surface condensers attacks the brass and copper tubes and fittings, and deposits the copper on the tubes of the boiler, although in only small quantities; and it is interesting to note that the green spots due to the presence of the copper are all on the under side of the scale—that is, in contact with the metal of the boiler tubes, showing that in all probability it had been deposited, as suggested, from the water in the boiler, and in contact with the iron would set up local galvanic action and tend to produce pitting.

The importance of preventing boiler incrustation, and thereby saving the enormous waste of fuel and injury which it entails, has not been without influence on the minds of inventors, and almost every conceivable substance, from potato-parings to complex chemical reagents, have from time to time been patented for this purpose, but have failed more or less for marine boilers, because either they have had an injurious effect upon the metal of the plates, or else have produced an enormous bulk of loose deposit, which, although easily cleaned out if the various parts of the boiler were accessible, and if it were only being used intermittently, yet in a marine boiler continuously working, rapidly chokes the portions between the tubes.

For these reasons, no treatment of the sea water in the boilers themselves is practically possible, and with high-pressure tubular marine boilers the water must be either condenser water, made up to the required bulk with distilled water, as is at present done, or else the condenser water must be augmented by sea water specially prepared for the purpose in a separate apparatus before being supplied to the boilers.

If the engines of a vessel are in good condition, she will approximately require 1 ton of water per 1000 horse power per twenty-four hours, to make up the volume of the condenser water to the amount required for the boilers, so that, even supposing the engines not to be in good order, and considerable waste to take place, 10 tons per diem would be an outside allowance for even very large vessels. To obtain this amount of treated sea water the author proposes an arrangement, full details and diagram being given in the original paper.

The sea water, containing 40 pounds of soda crystals to the ton is heated up under pressure in a separate apparatus by passing through the solution superheated steam. Under these conditions the precipitated mixture of calcium and magnesium carbonates becomes very dense and settles very quickly. The water is then forced through filtering frames into the hot well of the boiler and is then ready for use. The whole process is effective and rapid, and simple arrangements are made for flushing out the apparatus, after each batch of water.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

CAMBRIDGE.—The courses of science lectures this term are as numerous as usual, but present few noteworthy features. Mr. Gardiner gives a general course of Botany, while Mr. Darwin is conducting the course of Elementary Biology (Plants), the lectures being given in the Archæological Museum Lecture Room. Prof. Macalister is lecturing on the History of Human

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